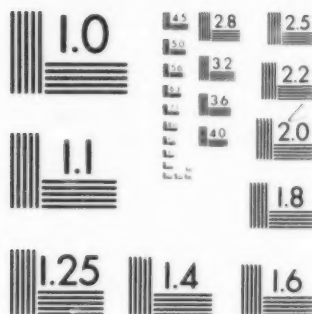


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Chemical Vapour Deposited Coatings for
High Temperature Corrosion Resistance

FINAL REPORT

BY

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S U M M A R Y

The application of anti-corrosion, abrasion-resistant coatings on low cost substrate materials such as mild steel, offers an attractive alternative to the use of expensive alloys which are required for some components of fossil energy conversion systems. Chemical vapour deposition (CVD) is a means of producing a number of refractory coatings, such as titanium diboride (TiB_2), which may provide the necessary protection from the hostile environments generated by fossil energy conversion.

The experimental conditions required to form titanium diboride (TiB_2) coatings on coupons of 1045 carbon steel sheet, were investigated in Phase I of this project, completed in March 1982. In Phase II, begun in September 1982, cylindrically-shaped specimens of 1045 steel were coated with TiB_2 . Sublayers of electrodeposited nickel and titanium carbide as well as controlled slow cooling were required to prevent flaking of the coating.

Tests being conducted on these specimens at the Physical Metallurgy Research Laboratories of CANMET indicate that TiB_2 coatings applied by CVD provide good protection against corrosion by sulphurous gases at 800°C .

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Chemical Vapour Deposited Coatings for High Temperature Corrosion Resistance.

1. INTRODUCTION

The service life of components exposed to the hostile environments existing in fossil-energy conversion systems such as coal-fired fluidized beds and coal-liquefaction reactors, can be prolonged by the use of protective coatings. For example titanium diboride (TiB_2) coatings applied by Chemical Vapour Deposition (CVD), have proved effective in protecting letdown valves in experimental coal-liquefaction reactors ⁽¹⁾.

In 1982, Ontario Research Foundation completed an investigation on behalf of the Department of Energy, Mines & Resources, and the National Research Council ⁽²⁾, to produce and evaluate TiB_2 coatings applied by CVD on small, rectangular coupons of various alloy sheet materials. In general, the coatings provided excellent corrosion resistance against sulphuric acid solutions ⁽³⁾ over most of the coupon area, but flaking which occurred at edges and sharp corners, prevented elevated-temperature corrosion testing in sulphurous gases, from being carried out at PMRL.

This project which was initiated in September 1982 and completed in March 1983, was undertaken to produce twelve fully-coated specimens for elevated-temperature corrosion testing at PMRL.

2. EXPERIMENTAL PROCEDURE

2.1. Specimen Shape

In order to eliminate the edge effect, a cylindrical specimen shape was adopted. Initially, the dimensions were as shown in Fig. 1, but later they were modified to those of Fig. 2. The specimen was supported in the reaction chamber by means of a thermocouple inserted in the axial hole.

2.2. Materials

The substrate material was 1045 carbon steel rod.

The chemical used were:

- Titanium tetrachloride purified liquid supplied by Fischer Scientific.
- Boron trichloride bottled liquid with a vapour pressure of 4.4 psig at 20°C and 7.0 psig at 24°C, supplied by Matheson.
- Methane, ultra-high purity (99.97% min.), supplied by Matheson.
- Hydrogen, prepurified (99.95% min.), supplied by Matheson.
- Argon, prepurified (99.998% min.), supplied by Matheson.
- Nitrogen, high purity (99.99% min.), supplied by Matheson.

2.3. Substrate Surface Preparation

The surface preparation of the machined specimens was as follows:

- Polishing with a 240-grit paper.
- Sand blasting with 36-grit fused-alumina particles, at 95 psig.
- Cleaning in an ultrasonic bath.
- Plating with 10µm of dull nickel (by Precious Plate Ltd).

2.4. CVD Coating Procedure

The coating system is shown schematically in Fig. 3.

In preparation for coating, the specimen is mounted on a stainless-steel sheathed thermocouple and inserted in the reaction chamber, as shown. The end caps are fitted, and the entire system, including the flow meters and gas connections, is pressure-tested with argon at 2 psig for 2 min. Then it is flushed with argon at a rate of about 30ml/min. After 2 hrs., argon is replaced by hydrogen flowing at a rate of 890ml/min., and the furnace is turned on.

When the specimen temperature reaches 927°C, usually after about 80 min., the hydrogen is diverted to bubble through the $TiCl_4$ bath maintained at 24°C and CH_4 is introduced. This continues for about 30 minutes, during which time a TiC coating approximately 15µm thick is deposited. The conditions for TiC deposition are summarized in Table I.

About 12 minutes before TiC coating is due to be completed, the TiCl_4 bath temperature is raised to 45°C in preparation for TiB_2 deposition. When TiC coating is completed, the methane valve is closed, the BCl_3 valve is opened, and a flow of BCl_3 of approximately 6.9 ml/min. is maintained for between 30 and 60 min. The operating parameters for depositing TiB_2 are summarized in Table 2.

On completion of the TiB_2 deposition, the TiCl_4 and BCl_3 are shut off, and the hydrogen flow rate is reduced from 890 to about 15 ml/min. The specimen is then cooled at about $1^\circ\text{C}/\text{min.}$ by gradually reducing the voltage of the furnace power supply. This is accomplished by means of a Variac transformer controlled by a motorized chain drive mechanism.

3. RESULTS AND OBSERVATIONS

3.1. Cold-wall System

In the initial experiments, specimen heating was accomplished by means of a Lepel 7.5 kW induction generator coupled to a susceptor of the same external dimensions as that used in the previous investigation⁽³⁾, but with a circular rather than a square aperture. Cylindrical specimens were coated directly with TiB_2 , but the coatings spalled severely during cooling. Improved adhesion was achieved by employing an intermediate layer of TiC, but an even greater improvement resulted from electrolytically plating the specimen with a dull nickel coating before depositing the TiC. Nevertheless, random spalling, or flaking, was evident on all the specimens. It was found that slower cooling rates improved coating adhesion. Because slow uniform cooling could not be achieved with induction heating, resistance heating was employed. This had the advantage of slow controlled cooling, but at the cost of some reaction occurring on the quartz reaction chamber wall, which caused cracking of the quartz tube. Therefore, a stainless steel reaction chamber was used in experiments D17 through D42.

3.2. Hot-wall System

All the specimens produced for hot-corrosion testing at PMRL were coated in the hot-wall system shown schematically in Fig. 3. In total, 41 specimens were coated, some without the nickel or TiC layers, to

investigate whether or not the slow cooling rate would eliminate the need for multiple-layers (Ni, TiC and TiB_2). Of these, 16 specimens were submitted to PMRL. The specimen identifications, and some of the relevant experimental parameters are shown in Table 3.

4. DISCUSSION

4.1. Specimen Shape and Size

It was evident from the results of the previous investigation⁽³⁾ that adherent coatings of TiB_2 could not be deposited on the sharp edges of thin specimens. In areas where the coating was intact, it could withstand tensile but not compressive stresses. It is likely that the morphology of TiB_2 enabled the coating to separate along crystal boundaries under tensile stress, but the very high hardness of 3400 VHN (compared with 2400 VHN for WC) did not allow any plastic deformation to take place under compression.

Increasing the diameter of the specimen from 8 to 10mm appeared to reduce the effect of compressive stresses on the coating, (Fig.4), the coating quality from one end of the specimen to the other appeared to be improved also by reducing the length of the specimen to 20mm to conform with the weight limitation of 10g specified by PMRL.

4.2. Factors Contributing to Flaking

(a) Coefficient of Thermal Expansion

Compressive stresses are introduced into the coating primarily as a result of a larger difference between the coefficient of thermal expansion of TiB_2 (5.6-6.6 ppm/ $^{\circ}\text{C}$), and the substrate steel (10-12ppm/ $^{\circ}\text{C}$). The beneficial effect of having a transitional layer such as TiC (7.5 ppm/ $^{\circ}\text{C}$) has been demonstrated in this study. The advantage of the nickel layer (13.3 ppm/ $^{\circ}\text{C}$) is believed to be its ductility, although the exact mechanism for stress accommodation remains unclear.

(b) Cooling Rates

Rapid cooling of the specimen is detrimental to retention of the coating. Various cooling rates were tried, ranging from several degrees per minute produced by shutting off of the r.f. generator to about $1^{\circ}\text{C}/\text{min.}$ achieved by motorized control of the furnace power. The observations to date indicate that a cooling rate of less than $2^{\circ}\text{C}/\text{min.}$ is required.

Although the initial cooling rate of a specimen from the CVD reaction temperature is critical for retaining the coating intact, subsequent heating and cooling of the coated specimen appear to present no particular problem. The specimens subjected to hot corrosion testing at PMRL have withstood repeated heating and cooling cycles (between 800°C to room temperature) for 24, 48 and 72 hour periods. Subsequent leaching tests on a 10% H_2SO_4 aqueous solution at 50°C indicated dissolution of iron of varying amounts between 2 to 10 g/l over a 24 hr. period. Further work is required to confirm these preliminary test results.

(c) Coating Thickness

Thicker coatings tend to flake off more readily than thinner coatings, based on qualitative assessment of the overall results. It was noted in particular that minor cracks are more prevalent in the head region of the specimen, which always faces the on-coming rich gas mixture and consequently has a relatively thicker deposit compared with the tail end.

No systematic study was undertaken on this subject.

(d) Rate of Deposition

It is known that residual stress in coatings often result from too-rapid a coating rate (electroplating for example). Since the TiB_2 coating is carried out at 927°C , this effect may not be significant, but it remains a possibility.

The effect of deposition rate was not studied, because the time limitations made it impractical to experiment with diluted gas mixtures to re-establish optimum operating conditions.

4.3. Interface Quality

Examination of the Spalled Areas

Metallographic and SEM examinations revealed that separation of the TiB_2 coating usually occurred at the interface between TiC and TiB_2 as seen in Figures 5 through 7. The X-ray diffraction analysis, (Figure 8), also shows that the outer surface of the coating is clearly TiB_2 , and the interface composition between TiB_2 and TiC coatings is a complex mixture of substances identified as, TiNi , TiB , and TiB_2 . There are additional peaks which could not be identified.

The lack of adhesion between the TiC and TiB_2 coatings could be due to two things:

- (A) a deficiency in boron
- (B) impurities in the interface between TiC and the unidentified materials

(A) Gas Mixture

The consistency of the BCl_3 flow rates were checked as was the possibility of a surge in the TiC flow rate caused when the bath temperature was increased from 25 to 45°C during start-up.

The optimum gas mixture having a B/Ti ratio of 1:3 (established in the previous investigation), was never seriously questioned. The lack of adhesion was thought to be primarily a result of contamination of the reactants by oxidation or other contaminants. Loss of reactants due to oxidation caused by leaks in the system had been identified and corrected a number of times, but did not explain the inconsistent and transitory nature of the problem which occurred only at the beginning of TiB_2 deposition.

(B) Impurity Effects

There is now strong evidence to suggest that the BCl_3 vapour, in contact overnight with Teflon and Tygon tubing in many locations, changes its composition. The contaminated gas is the first to enter the reaction chamber, but the phenomenon is temporary, because this contaminated vapour is used up in the process and a stream of

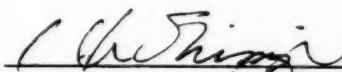
fresh vapour emerges from the storage bottle. This conclusion, supported by the observation that it had not been possible to coat two specimens successfully, in succession, was arrived at near the end of this project. However, the last several specimens were coated successfully by purging the BCl_3 line prior to deposition, indicating that the contamination of BCl_3 is the most detrimental factor effecting the TiC/TiB_2 interface bond strength. It has now been possible to coat steel blocks with sharp corners with TiB_2 by purging the BCl_3 line.

5. CONCLUSIONS

1. Gross flaking of TiB_2 coatings applied to mild steel by CVD, can be prevented by employing intermediate layers of electro-deposited nickel and TiC .
2. Slow cooling from the deposition temperature to near room temperature, appears to be an additional requirement for avoiding flaking.
3. The coating thus produced can be subjected to repeated heating and cooling, subsequently, without flaking.
4. One of the critical factors controlling the adhesion of TiB_2 to the TiC intermediate coating, is the quality of the BCl_3 gas, which must be kept free from degradation.



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Final Report

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- (2) Protective Coatings for Components of Fossil Energy Conversion Systems, DSS Contract, Serial Number 1SQ81-00070, CANMET Project Number 43090203.
- (3) W. Sze, H. Shimizu and W.M. Gibbon, Final Report, August 1982, DSS Contract 1SQ81-00070.

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- Table 1 : Operating Conditions for TiC Deposition
- 2 : Operating Conditions for TiB₂ Deposition
- 3 : Details of Experiment of Parameters for each Specimen

Final Report

TABLE 1.

Operating Conditions for TiC Deposition

Substrate	:	1045 carbon steel
Specimen	:	cylindrical, with rounded ends
Deposition Temperature	:	927°C
Gas Flow	:	H ₂ 890 ml/min.
		CH ₄ 55 ml/min.
		TiCl ₄ (e) 11.4 ml/min. @ 24°C

TABLE 2.

Operating Conditions for TiB₂ Deposition

Substrate	:	1045 carbon steel
Specimen	:	cylindrical, with rounded ends
Deposition Temperature	:	927°C
Gas Flow	:	H ₂ 890 ml/min.
		BCl ₃ (g) 6.9 ml/min.
		TiCl ₄ (e) 34.2 ml/min. @ 45°C

Details of Experiment of Parameters for each Specimen

** Sent to PMRL

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2(B) : A TiB_2 Coated Specimen
- Figure 3 : Hot-wall CVD System
- Figure 4 : Effects of Specimen Diameter and Length on Coating Adhesion.
- Figure 5 : SEM Examination of Flaked Region
- Figure 6 : Partially flaked TiB_2 Coating.
- Figure 7 : Separation of TiB_2 Coating from TiC .
- Figure 8 : X-ray Diffraction Patterns of Flaked and Unflaked Regions.

BULLET SHAPED SAMPLE

Scale : 4 : 1

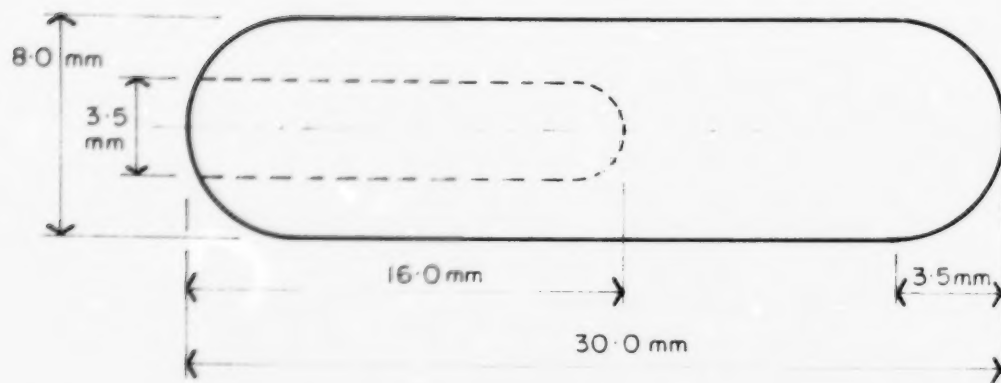


FIGURE 1(A) : Dimensions of Preliminary CVD Specimen.



FIGURE 1(B) : A TiB₂ Coated Specimen.

BULLET SHAPED SAMPLE

Scale: 5:1

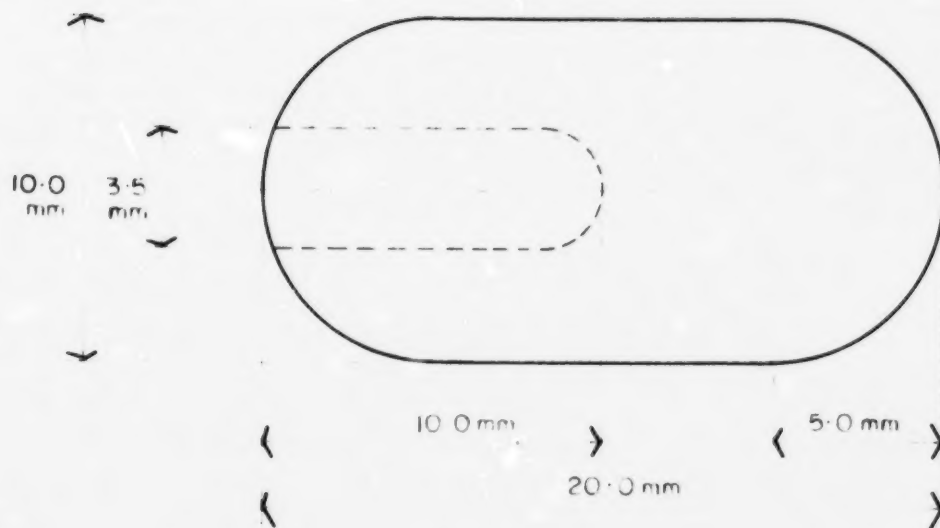


FIGURE 2(A) : Dimensions of Final CVD Specimen.



FIGURE 2(B) : A TiB₂ Coated Specimen.

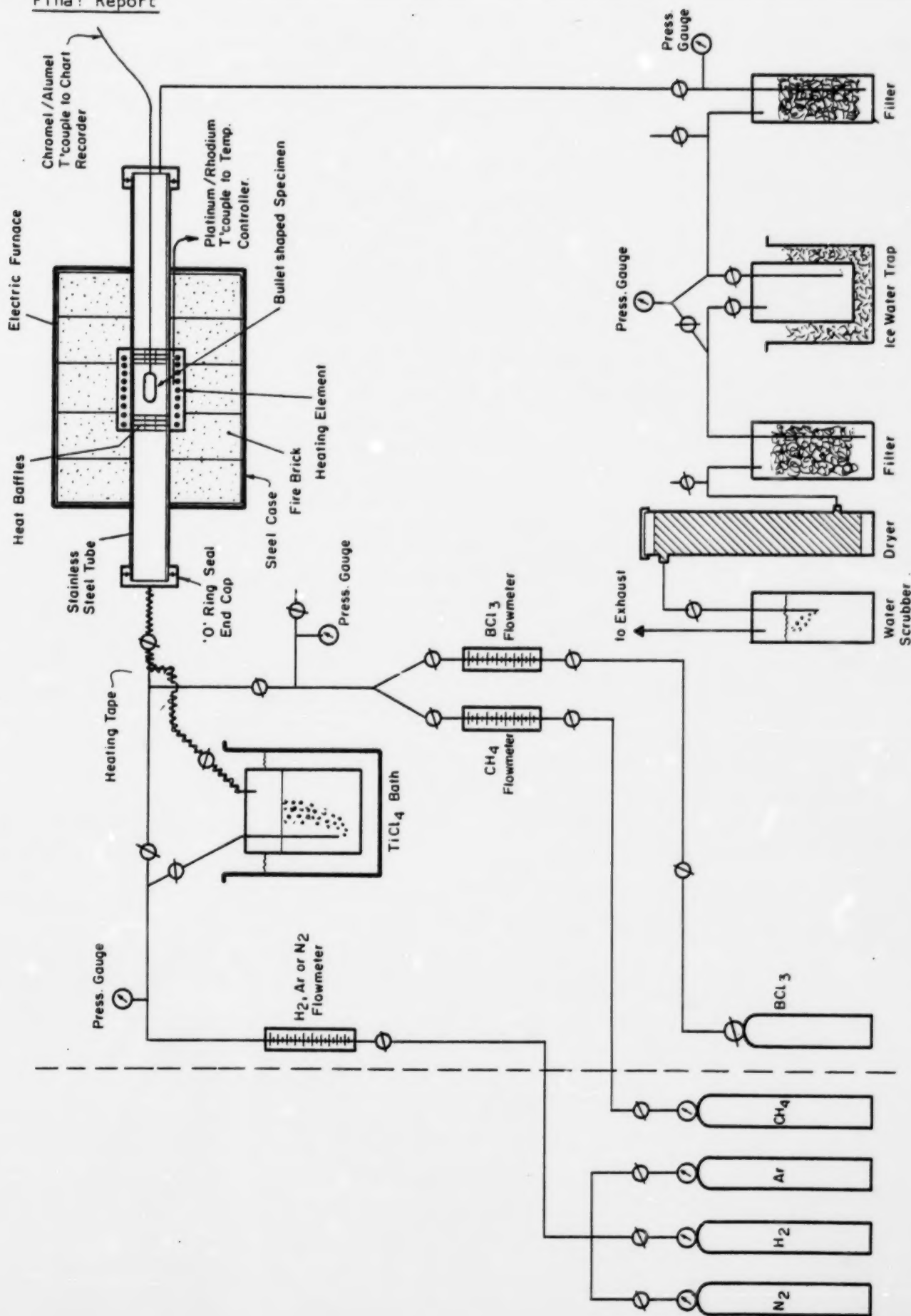


FIGURE 3. HOT WALL CVD SYSTEM



FIGURE 4 : Effects of Specimen Diameter and Length on Coating Adhesion.

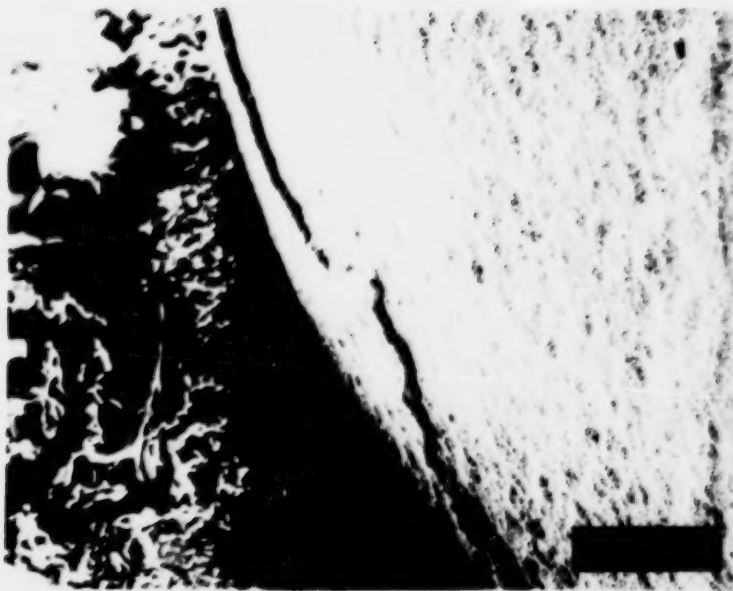


FIGURE 5 : SEM Examination of Flaked Region.

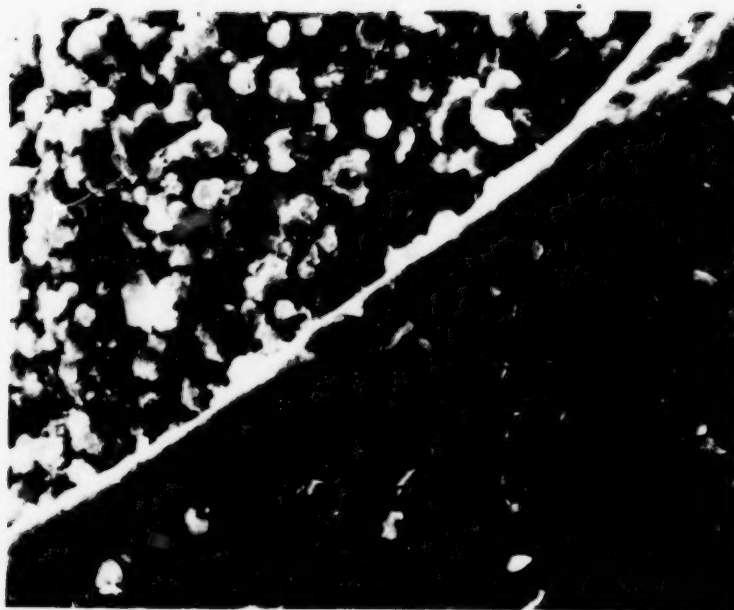


FIGURE 6 : Partially flaked TiB_2 Coating.



FIGURE 7 : Separation of TiB_2 Coating from TiC .

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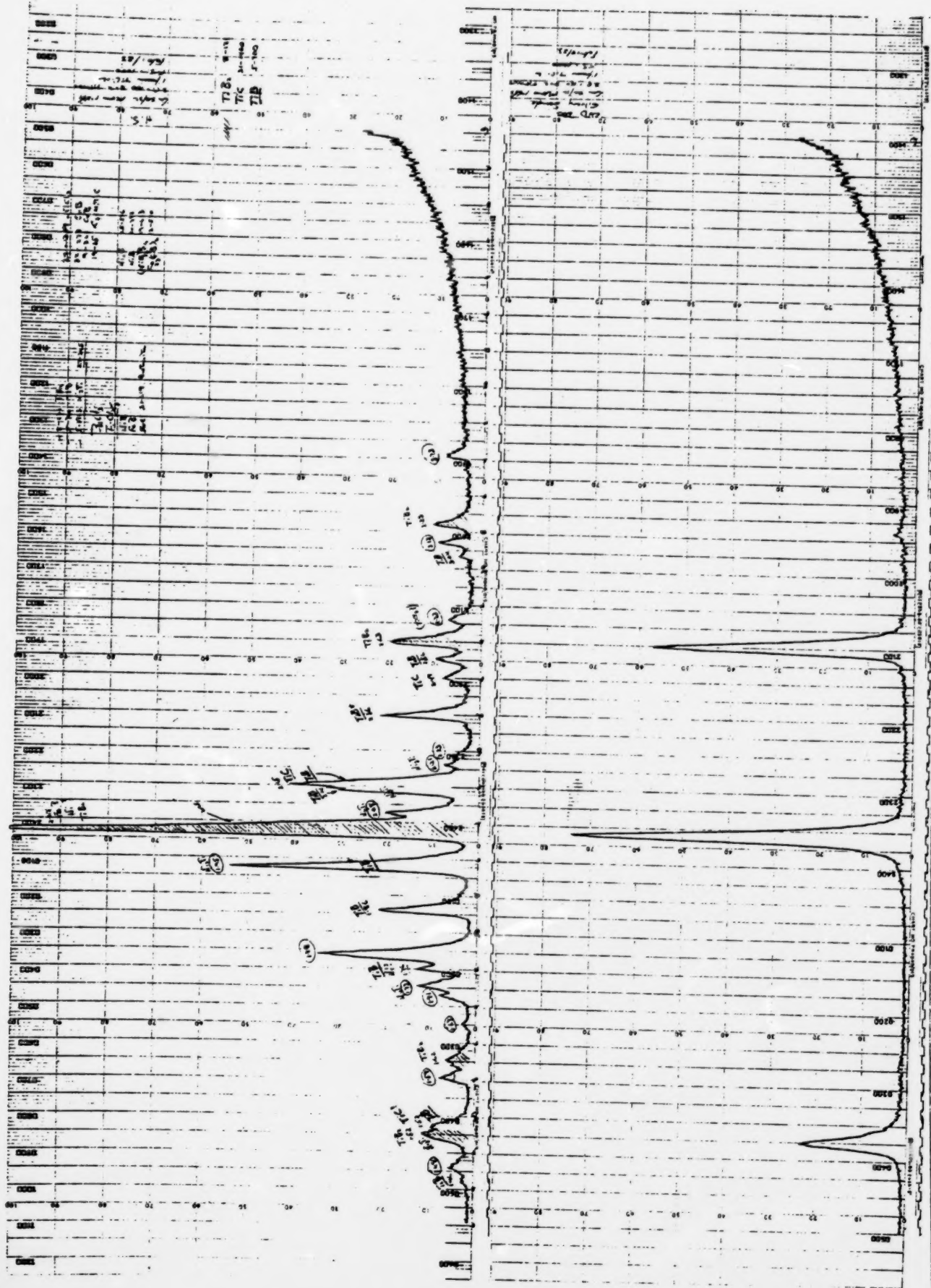


FIGURE 8 : X-Ray Diffraction Patterns of Flaked and Unflaked Regions.